Experimental Section

General Methods. All operations were carried out under an inert atmosphere. The ^{1}H, ^{11}B and ^{13}C NMR spectra were plotted on a Varian Gemini-300 spectrometer with a Nalorac-Quad probe. Mass spectra were recorded using with a Hewlett Packard 5989B mass spectrometer/5890 series II gas chromatograph or a Finnigan mass spectrometer model 4000. CI gas used was isobutane. The optical rotations were measured using a Rudolph Autopol III polarimeter.

Materials. Anhydrous ethyl ether (Et_2O) purchased from Mallinckrodt, Inc. was used as received. CH_2Cl_2 was distilled over CaH_2. 2-Carene, borane-methyl sufide complex, allylmagnesium bromide, 1-heptyn-3-ol, Lindlar's catalyst, triethylamine trihydrofluoride, and acryloyl chloride were all obtained from the Aldrich Chemical Co. Grubbs' catalyst was obtained from Strem Chemicals.

Optical Upgradation of 2. (*S*)-1-Heptyn-3-ol of 74% ee was prepared via Alpine-Borane reduction of the corresponding ketone.[9] 3,5-Dintirobenzoyl chloride (6.9 g, 30 mmol) was added to the above alcohol (2.24 g, 20 mmol) dissolved in CH_2Cl_2 (40 mL). The flask was cooled to 0 ^{o}C, followed by the addition of Et_3N (6 g, 60 mmol). The mixture was stirred at rt for 2 h, filtered through a pad of silica, concentrated and chromatographed over silica (hexanes: EtOAc:: 98:2) to obtain 5.0 g (80%) of the dinitrobenzoate. This was recrystallized twice in hexanes.

The above 3,5-dinitrobenzoate (3.1 g, 10 mmol) was dissolved in 10 mL of methanol and stirred at 0 ^{o}C for 2h with 4 mL of 3N NaOH. Quenching the reaction with dilute HCl (1%, 50 mL), followed by extraction with pentane (3x50 mL), purification through silica gel, and concentration provided 0.94 g (84%) of optically pure (*S*)-1-heptyn-3-ol, as determined by HPLC analysis of its 3,5-dinitrobenzoate on a CHIRALCEL OD-H column.

Preparation of 5. (*S*)-1-Heptyn-3-ol (4.96 g, 21.85 mmol) was dissolved in 50 mL of THF and cooled to –78 °C, followed by the dropwise addition of 10.5 mL of *n*-BuLi (2.5 M in hexanes, 26.25 mmol). The solution was stirred for 10 min, followed by the addition of DMF (3.19 g, 43.7 mmol) and continued stirring for an additional hour. The reaction was then brought to 0 °C and quenched with aqueous dilute HCl (1%, 100 mL). The product was extracted with Et_2O (3x50 mL), dried ($MgSO_4$), concentrated, and chromatographed over silica (hexanes:EtOAc::99:1). Yield: 2.89 g, 52%.

Preparation of 6. Aldehyde **5** (1.9 g, 7.48 mmol) was dissolved in 20 mL of THF and 0.5 g of Lindlar catalyst was added. The reaction flask was purged with hydrogen and closed under a positive pressure of hydrogen. The reaction was monitored by the consumption of hydrogen using a gasimeter. Upon completion (~10 h), the reaction mixture was filtered through a silica gel pad, the solvent was removed, and purified by silica gel column chromatography (hexane:EtOAc::98:2) to afford 1.24 g (65%) of **6** as a liquid.

Preparation of 8. Allylmagnesium bromide (9 ml, 1.0 *M*, 9 mmol) was added dropwise to a well-stirred solution of *B*-methoxydiiso-2-caranylborane (3.16 g, 10 mmol) in Et_2O (10 ml) at -78 °C. The mixture was then stirred for 0.5 h at -78 °C, allowed to warm to rt, and stirred for 4 h. The solvent was removed under aspirator vacuum, the residue was extracted with pentane (3 x 150 ml), filtered through a Kramer filter,[18] and concentrated to afford Icr_2BAll (**7**) (^{11}BNMR δ 79 ppm) in essentially quantitative yield. 6 Mmol of the above $^{l}Ipc_2BAll$ was dissolved in Et_2O to make Et_2O-pentane (1:1) and cooled to -100 °C. A solution of **6** (1.28 g, 5 mmol) in anhydrous Et_2O (5 ml) was added dropwise and the reaction mixture was stirred at –100 °C for 1 h when the reaction was complete (^{11}B NMR shift from δ 79 to δ 52 ppm). Addition of methanol (1 ml) to this intermediate, followed by the usual work up with NaOH and H_2O_2 afforded the

crude product which was extracted with Et_2O, washed with brine, and dried over anhydrous $MgSO_4$. The pure product was separated from isopinocampheol by silica gel column chromatography (hexane:ethyl acetate::95:5) to obtain 1.18 g (79%) of **8** as a liquid.

Preparation of 11. 2.98 g (10 mmol) of **8** was dissolved in 20 mL of CH_2Cl_2, cooled to 0 •C, and 1.35 g (15.0 mmol) of acryloyl chloride and 3.0 g (30 mmol) of Et_3N were added, warmed to rt and stirred for 4 h. The resulting mixture was filtered through a short pad of celite to remove solid Et_3N•HCl, poured into water, and the product extracted with CH_2Cl_2. The crude product was purified by silica gel column chromatography (hexane:ethyl acetate:: 99:1) and concentrated to obtain 2.7 g (77%) of **9**. Grubbs' catalyst (0.16 g, 0.02 mmol, 10 mol%) was dissolved in 5 mL of CH_2Cl_2 and was added dropwise to a refluxing solution of the above acrylic ester (0.7 g, 2 mmol) in 200 mL of CH_2Cl_2. Refluxing was continued for 12 h by which time all of the starting material was consumed (TLC). The solvent was removed under aspirator vacuum and the crude product was purified by silica gel column chromatography (hexane:ethylacetate::80:20) to obtain 0.54g (84%) of **11**.

Preparation of 1a. Lactenone **11** (0.32 g, 1 mmol) was dissolved in 4 mL of CH_3CN and Et_3N-HF (1.2 g, 8.0 mmol) was added. The mixture was stirred for 12 h, worked up with EtOAc (3x25 mL), dried ($MgSO_4$), concentrated, and chromatographed over silica (hexanes:EtOAc::6:4) to provide 0.2 g (94%) of **1a**.

Preparation of 1b. Compound **1a** (0.1 g, 0.5 mmol) was dissolved in 1 mL CH_2Cl_2, followed by the addition of Ac_2O (0.1 g, 1 mmol) and pyridine (0.16 g, 2 mmol). The mixture was stirred for 15 h, concentrated, and chromatographed over silica (hexanes:EtOAc:: 8:2) to provide 0.12 g (98%) of umuravumbolide.